

# PATENT SPECIFICATION

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- (21) Application No. 53415/73 (22) Filed 16 Nov. 1973  
(23) Complete Specification filed 5 Nov. 1974  
(44) Complete Specification published 1 Sept. 1977  
(51) INT CL<sup>2</sup> C02B 1/20; C02C 5/02  
(52) Index at acceptance C1C 215 217 253 311 400 40Y 440  
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## (54) COMPOSITION FOR TREATMENT OF WASTE WATERS AND PROCESS FOR MAKING SAME

(71) We, ALCAN RESEARCH AND DEVELOPMENT LIMITED, a Company incorporated under the laws of Canada, of 1, Place Ville Marie, Montreal, Quebec, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a composition for the treatment of waste waters and in particular it relates to a product for removal of entrained colloidal solids.

It is already well known that waste waters, which are to be discharged into water courses or lakes, should be treated so as to reduce entrained solids and to reduce the content of soluble phosphorus compounds, such as phosphates, to a low value in order to reduce pollution hazards. It is already well known to add aluminium sulphate, which has a flocculating or coagulating effect on entrained solids and which is also effective to reduce dissolved phosphates to a very low level.

The present invention has for its principal object the production of a material for water treatment comparable in effectiveness with aluminium sulphate, but which can be produced at lower cost by reason of its production from a waste material, which itself poses certain disposal problems.

In the Bayer process for the production of alumina from bauxite, large quantities of so-called "Red Mud" are separated from the digestion liquors. In addition to the iron compounds, which give it its colour, fine particle size Red Mud includes substantial quantities of sodium aluminium silicates, which are primarily in the form of sodium aluminium silicates, which are primarily in the form of the so-called desilication product, an easy-to-react zeolite type compound of the formula:



In accordance with one aspect of the present invention a composition for the treatment of waste waters comprises the reaction product of a Red Mud which includes 12—20%  $\text{Al}_2\text{O}_3$ , 8—14%  $\text{Na}_2\text{O}$ , 12—20%  $\text{Fe}_2\text{O}_3$ , 12—20%  $\text{SiO}_2$  and 10—15%  $\text{TiO}_2$  with sulphuric acid, which may contain 0—200 parts hydrochloric acid per 100 parts of sulphuric acid (by weight), in an amount of 65—120 parts of sulphuric acid and hydrochloric acid by weight per 100 parts of Red Mud (dry basis). The reaction of the sodium aluminium silicate desilication compound with acid leads to the formation not only of sodium alum, but also to the formation of an active silica gel which plays an important part in the eventual water treatment operation.

For ease of dispersion in the water to be treated the product should be in a friable condition, without necessarily being wholly dry. In order to obtain the product in this condition without requiring to apply heat for moisture evaporation purposes at the end of the reaction, the amount of water introduced into the reaction mixture at the beginning of the reaction is controlled so as to be only sufficient to permit the Red Mud solids to be thoroughly mixed with the acid. Ordinarily the initial water content of the reaction mix should be less than 100 parts water per 100 parts Red Mud solids. As the reaction between the acid and

the Red Mud solids proceeds, a considerable part of the water evaporates, while the remaining part is taken up in the formation of compounds, such as hydrated silica gel and as water of crystallisation of sodium alum and iron sulphates. In consequence the originally slurried reaction mixture sets into a friable mass which can easily be reduced to a relatively small particle size.

The reaction between the acid and the Red Mud solids in the highly acid conditions is highly exothermic and is essentially completed in about 10 minutes. However, it is preferred to hold the reacted mass at about 140—150°C for about 1 hour in order for greater dehydration of the reaction product to occur, thus permitting easier grinding of the solidified mass. Although the product of the present invention may be produced by reacting a slurry of Red Mud with concentrated sulphuric acid, it may be also conveniently produced by slurrying dry Red Mud with relatively dilute sulphuric acid of about 30% strength. Such relatively dilute acid is frequently available as a waste product from spent pickling baths. This relatively cheap source of sulphuric acid may be supplemented by hydrochloric acid of similar strength, which may also be obtained relatively cheaply, as compared with concentrated sulphuric acid. Thus the process for producing the product of the present invention may be based essentially on industrial effluents, which would themselves otherwise require disposal. Products of somewhat different effectiveness can be produced by variation of the relative proportions of acid to Red Mud and also by the substitution of part of the sulphuric acid by hydrochloric acid. However, the relative proportions of the reactants are not very critical and useful products can be obtained through a wide range of relative proportions of Red Mud solids to acids. Small variations of the relative proportions do not lead to ill-effects. In addition to sodium alum and silica gel already mentioned the reaction product includes some iron sulphates and, when the acid contains hydrochloric acid, some aluminium trichloride and ferric trichloride. All of these compounds are known to have beneficial effect in the treatment of waste waters.

In order to exemplify the production of products in accordance with the present invention Red Mud, in the form of particles of essentially -65 (B.S.S.) mesh and of the chemical composition indicated above was reacted with varying amounts of sulphuric acid or sulphuric acid/hydrochloric acid mixtures as follows:—

- (F—1) 1:1 Red Mud/water slurry was reacted with concentrated  $H_2SO_4$  in the weight proportions of 100 parts of Red Mud (dry basis):75 parts of  $H_2SO_4$ .
- (F—2) 1:1 Red Mud/water slurry was reacted with concentrated  $H_2SO_4$  in the weight proportions of 100 parts of Red Mud (dry basis):90 parts of  $H_2SO_4$ .
- (F—2A) Dry Red Mud was reacted with a mixture of concentrated  $H_2SO_4$  and 35% HCl, in the weight proportions (pure reagent basis) of 100 parts Red Mud:25 parts of  $H_2SO_4$  and 50 parts of HCl.
- (F—3) 1:1 Red Mud/water slurry was reacted with concentrated  $H_2SO_4$  in the weight proportions of 100 parts Red Mud (dry basis):110 parts of  $H_2SO_4$ .

In all cases the reactants were mixed rapidly for 5—10 minutes until a friable solid mass was obtained. Then, to finish off the reaction the mix was held for about 1 hour at 150°C.

In general, 1 part of Red Mud (dry basis) yields about 2 parts of relatively dry, friable solids after 5—10 minutes of mixing. Prolonged drying of the mix at 105°C results in a further reduction of moisture in the product so that finally one may obtain only 1.5 parts of product from 1 part of dry Red Mud.

All the above formulations give somewhat acidic reactions when the respective products are placed in water, e.g. 20-g samples of F—1, F—2 and F—3 in 1-litre of water gave the following pH values: 3.8, 3.1 and 2.8 respectively.

The extent of the reaction of  $Al_2O_3$  and  $Fe_2O_3$  present in Red Mud in unreacted form or as silicates depends on the amount of the acid used. Typical percentages of water soluble compounds obtained from 100-g of Red Mud (dry basis) are given in Table I below. The water-insoluble portion varies between 15 and 25%. This includes active silica gel, as well as  $TiO_2$  and unreacted portions of  $Fe_2O_3$  and  $Al_2O_3$ .

TABLE I

WATER SOLUBLE COMPOUNDS IN ALUMIZED RED MUD SOLIDS (ARMS)  
(in g/100 g of Dry Red Mud)

Formula	Al +++ as $Al_2O_3$ , gms.	Na+ as $Na_2O$ gms.	Fe+++ as $Fe_2O_3$ , gms.	$SO_4$ gms.
F-1	13.8	11.8	0.5	68.1
F-2	15.1	12.1	4.5	87.5
F-3	17.3	11.6	9.9	100.0

The relative effectiveness of F-1 and F-2 alumized Red Mud solids in removing soluble phosphates, together with the corresponding pH changes of the treated sewage water are given in Table II, whereas Table III gives comparative results for F-2 and F-2A solids alongside with such well-known water treating agents as aluminium sulphate, bauxite alum and lime.

TABLE II

REMOVAL OF PHOSPHORUS FROM SEWAGE WATER BY F-1 AND F-2 ARMS

Reagent Used	Amount Added (grl)	Water Before Treatment		Water After Treatment	
		pH Value	P(ppm)	pH Value	P(ppm)
F-1	0.1	7.4	8.2	7.3	0.8
	0.2	7.4	8.2	7.1	0.2
	0.3	7.4	8.2	6.9	0
	0.4	7.4	8.2	6.7	0
F-2	0.2	7.4	8.2	6.9	0
	0.3	7.4	8.2	6.8	0
	0.4	7.4	8.2	6.6	0

TABLE III

SHOWING THE COAGULATING AND PHOSPHORUS REMOVAL POWER OF F-2 AND F-2A ARMS IN COMPARISON WITH  $Al_2(SO_4)_3$  BAUXITE ALUM AND LIME

Test	Reagent Used	Amount Added (gpl)	Solids in Effluent (Supernatant) (ppm)	Phosphorous in Effluent (ppm)
A	Blank (control)	0.0	33	4.6
	F-2	0.2	8	0.9
	F-2A	0.2	14	0.6
	Aluminium sulphate	0.2	11	0.6
	Lime	0.3	30	0.7
B	Blank (control)	0.0	9	4.6
	F-2	0.2	1.0	1.0
	F-2	0.3	0.5	0.8
	Bauxite Alum	0.2	3.0	0.8
	Bauxite Alum	0.3	2.0	1.0
	Aluminium sulphate	0.2	5.0	0.6

The results shown in Table II indicate that additions of F-1 ARMS in amounts of 0.3 gpl or more and as little as 0.2 gpl of F-2 ARMS are capable of removing more than 8 ppm of phosphorus from sewage waters.

The comparative data given in Table III shows that weight-for-weight F-2 ARMS are as good in their action as coagulating and phosphorus removing agents as the usual well known water treating agents, e.g. aluminium sulphate, bauxite alum or lime.

TABLE IV  
TYPICAL COMPOSITION OF ALUMIZED RED MUD SOLIDS (ARMS)

Constituent	% by Weight
$\text{NaAl}(\text{SO}_4)_2 \cdot \text{XH}_2\text{O}$	60.1
$\text{CaSO}_4$	11.9
$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	4.7
$\text{FeSO}_4$	6.5
$\text{SiO}_2$	6.2
$\text{TiO}_2$	5.1
$\text{Fe}_2\text{O}_3$	5.4

WHAT WE CLAIM IS:—

1. A composition for the treatment of waste waters comprising the reaction product of a Red Mud, comprising:
  - 12—20% by weight Al expressed as  $\text{Al}_2\text{O}_3$
  - 8—14% by weight Na expressed as  $\text{Na}_2\text{O}$
  - 12—20% by weight Fe expressed as  $\text{Fe}_2\text{O}_3$
  - 12—20% by weight Si expressed as  $\text{SiO}_2$
  - 10—15% by weight Ti expressed as  $\text{TiO}_2$
2. A method of making a composition as claimed in Claim 1, which comprises reacting the acid with the Red Mud in an aqueous slurry.
3. A method as claimed in Claim 2, wherein the amount of water in the reaction mixture is less than 100 parts by weight per 100 parts by weight Red Mud solids.
4. A method as claimed in either Claim 2 or Claim 3, wherein the reacted reaction mixture is heated to a temperature of from 140 to 150°C.
5. A method as claimed in either Claim 2 or Claim 3, wherein the reacted reaction mixture is held at from 140 to 150°C for about 1 hour.
6. A method as claimed in any one of Claims 2 to 5, wherein the reaction is performed by slurring substantially dry Red Mud with an aqueous solution of the acid.
7. A method as claimed in Claim 6, wherein the acid is sulphuric acid at a concentration of about 30% by weight.
8. A method as claimed in any one of Claims 2 to 7, wherein the Red Mud is in the form of particles of -65 mesh.
9. A method as claimed in any one of Claims 2 to 8 and substantially as hereinbefore described in any one of Examples F—1 to F—3.
10. A composition as claimed in Claim 1 whenever made by the process claimed in any one of Claims 2 to 9.
11. A method of treating waste water comprising contacting the waste water with a composition as claimed in either Claim 1 or Claim 10.
12. Water whenever treated by the method claimed in Claim 11.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1977.  
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.